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Energy Procedia 37 (2013) 1736 – 1743

Energy Procedia

GHGT-11

# Modeling of binary and ternary VLE of the AMP/Pz/$H_2O$ system

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**Abstract**

The AMP/Pz system is industrially important but modeled VLE data are scarce. Reported data were used to develop a NRTL model representing binary VLE data of aqueous AMP and Pz solutions and ternary VLE data for aqueous AMP/Pz solutions at different temperatures and concentrations. The model represents very well the experimental results, but could be improved when more data are available in the parameter regression. The model shows that the activity coefficients of AMP are higher than those of Pz. The suggested binary interaction parameters can reasonably well predict the ternary system.



*Keywords:* VLE, AMP, Pz, NRTL, Absorption, Modeling.

## 1. Introduction

Amine based CCS is a viable and mature technology to remove $CO_2$ from gas streams. However drawbacks are energy and capital costs which should be reduced in order to bring the energy penalty down when used for post combustion $CO_2$ capture. One alternative is to develop new solvent systems with better mass transfer characteristics, higher stability toward

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doi:10.1016/j.egypro.2013.06.049

thermal and oxidative degradation, lower heat of absorption, high equilibrium temperature sensitivity and high cyclic capacity while still being benign to the environment.

AMP (2-amino-2-methyl-1-propanol), as a sterically hindered amine is an interesting chemical considering the low carbamate stability [1,2] combined with high equilibrium temperature sensitivity. Low carbamate stability is associated with formation of carbonate/ bicarbonate and therefore a reduction of the regeneration energy requirement might be possible.

Piperazine (Pz), as a cyclic diamine, has been reported to have fast mass transfer compared to most alkanolamines [3,4] and proposed as a promoter [5,6]. The blend of AMP and Pz has been recommended as a strong solvent candidate due to high cyclic capacity, comparably low heat of absorption and good equilibrium temperature sensitivity [7].

Binary/ ternary VLE data are essential to develop an accurate design of acid gas treatment processes and also crucial to develop rigorous thermodynamic models (e.g. e-NRTL or extended UNIQUAC). Some binary VLE data for the AMP/$H_2O$ system are available in the literature [8,9], whereas binary VLE data for the Pz/$H_2O$ system are very limited. The total pressure of Pz over water was reported [10] as well as the binary VLE at high pressure and temperature [11]. Recently, binary and ternary data of AMP/Pz/$H_2O$ VLE were reported based on ebulliometric experiments and using a combination of titration and $^1$H-NMR techniques to quantify the concentrations of each amine [12].

In this work, we focus on developing an NRTL model for the binary AMP/$H_2O$ and Pz/$H_2O$ and the ternary AMP/Pz/$H_2O$ systems. Only the activity coefficients ( $_i$ ), total pressures $(P_i)$ and mole fractions of vapor phase $(y_i)$ [12] were used for the parameter regression. However, still the data basis is limited and a more precise and robust model can only be obtained when more data are available.

## 2. Modeling Part

### *2.1.1. Activity coefficient model*

An NRTL model [13] was used to estimate the activity coefficients for the multicomponent system and can be written as:

$$\ln {}_i^{NRTL} \quad \frac{\sum_{j\ 1}^{N} {}_{ij}\ G_{ij}\ x_j}{\sum_{k\ 1}^{N} G_{ki}\ x_k} \quad \sum_{j\ i}^{N} \frac{x_j\ G_{ij}}{\sum_{k\ i}^{N} x_k\ G_{kj}} \quad {}_{ij} \quad \frac{\sum_{k\ 1}^{N} {}_{kj}\ G_{kj}\ x_k}{\sum_{k\ 1}^{N} G_{kj}\ x_k} \tag{1}$$

Based on previous work [14] for amine/alkanolamine system, the non-randomness parameter ( $_{ij}$ ) was fixed at a value of 0.2 and since $_{ij} \quad a_{ij} \quad b_{ij}/T$ the NRTL model requires 4 parameters $(a_{ij}, b_{ij})$ to be calculated.

### *2.1.2. Parameter regression*

The NRTL parameters were determined by using an in-house Matlab code for multi-response parameter estimation, Modfit [15], with the objective function as given by Eq. 2.

$$F \quad \sum_{i\ 1}^{n} \frac{{}^{Exp}_{\text{Amine}} \quad {}^{calc}_{\text{Amine}}}{{}^{Exp}_{\text{Amine}}}^2 \quad \sum_{i\ 1}^{n} \frac{P_{\text{Sol}}^{Exp} \quad P_{\text{Sol}}^{calc}}{P_{\text{Amine}}^{Exp}}^2 \quad \frac{y_{\text{Amine}}^{Exp} \quad y_{\text{Amine}}^{calc}}{y_{\text{Amine}}^{Exp}} \tag{2}$$

Deviations between model results and experimental data are expressed as absolute average relative deviations (AARD) according to Eq. 3.

$$AARD \quad \frac{1}{n} \sum_{i=1}^{n} \frac{\left| \text{model} - \text{exp} \right|}{\text{exp}} \qquad (3)$$

where represents the activity coefficient, total pressure of solution and vapor phase composition respectively.

## 3. Results and discussion

### *3.1. Binary VLE of AMP(1)/$H_2O$(3) model*

Fig. 1(a), 1(b) and 1(c) show the comparisons between the NRTL model representation and experimental data for total pressure, activity coefficient and composition for the binary VLE of the AMP/$H_2O$ system [12] respectively. It is seen that the NRTL model successfully represents the experimental data with the suggested parameters given in Table 1 along with absolute average standard deviations (AARD) in Table 2. The model shows that the activity coefficients of AMP increase with increasing temperature whereas they decrease with increasing concentration. The activity coefficient of water is relatively constant. AMP is observed to be more volatile than some of the other commercial solvents, such as MEA and MDEA [16]. The limited data material is visible also in the large standard deviations given in Table 2.

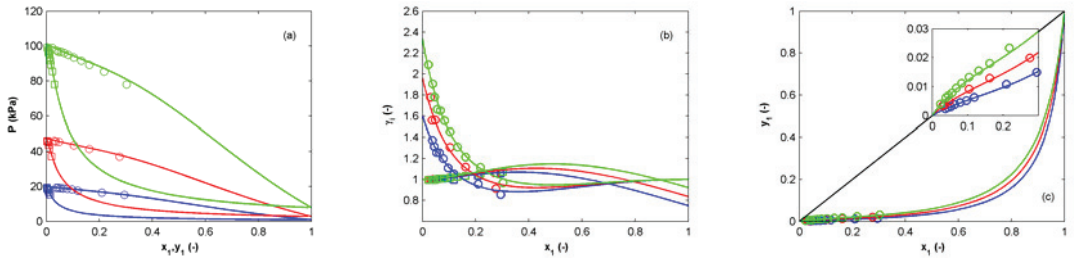


Figure 1. Model prediction for (a) PTxy data [12] (b) activity coefficients and (c) x/y data of the AMP/$H_2O$ system at 60 C, 80 C and 100 C.

Table 1. Binary interaction parameters for AMP/$H_2O$ and Pz/$H_2O$

| AMP(1)+$H_2O$(3) | | | |
|---|---|---|---|
| $a_{13}$ | -0.0146 ± 0.3 | $a_{31}$ | 2.944 ± 0.8 |
| $b_{13}$ | -671.117 ± 109 | $b_{31}$ | 190.099 ± 275 |
| Pz(2)+$H_2O$(3) | | | |
| $a_{23}$ | -6.875± 2 | $a_{32}$ | -22.629 ± 6 |
| $b_{23}$ | -1552.228 ± 761 | $b_{32}$ | -7536.951 ± 1931 |

Table 2. Absolute average relative deviations (AARD) of the NRTL model for AMP/$H_2O$ and Pz/$H_2O$ systems

| | AMP/$H_2O$ | | Pz/$H_2O$ | |
|---|---|---|---|---|
| | Exp. (N) | AARD (%) | Exp. (N) | AARD (%) |
| | 26 | 2.1 | 24 | 7.4 |
| P | 26 | 1.2 | 24 | 0.4 |
| y | 26 | 2.3 | 24 | 9.4 |

The given parameters in Table 1 also successfully predicts the binary VLE data from isobaric experiments [8] (Fig. 2a) as well as in static VLE experiments [9] (Fig. 2b). In addition, the model is able to predict the excess enthalpy data [17] reasonably well. Some over-prediction is seen for lower concentrations(x<0.3) in Fig. 3a. The freezing point depressions [18], however, are only predicted well for low concentrations in Fig. 3b. This indicates that the parameters could be improved by including more data from the literature during the parameter regression for instance the freezing point depression data.

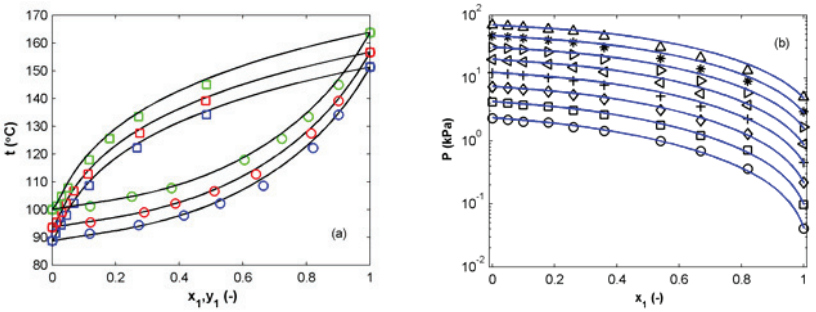


Figure 2. The NRTL model for (a) Isobaric measurements at 66.7, 80.0 and 101.3 kPa [8] and (b) Static measurements at 20-90 [9] of AMP/$H_2O$ system.

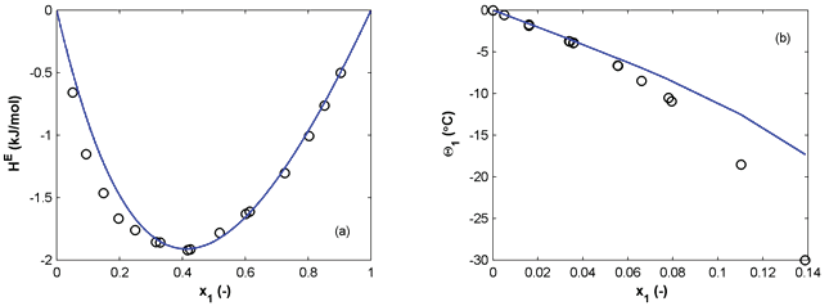


Figure 3. The NRTL model for (a) the excess enthalpy data at 35 C [17] and (b) the freezing point depression data [18] of AMP/$H_2O$ system.

### *3.2. Binary VLE of Pz(2)/$H_2O$(3) model*

Fig. 4(a), 4(b) and 4(c) show that the NRTL model successfully represents experimental data [12] with the suggested parameters in Table 1 along with absolute average standard deviations

(AARD) in Table 2. The activity coefficients of Pz are lower and less temperature sensitivity than that of AMP thereby Pz behaves less volatile than that of AMP.

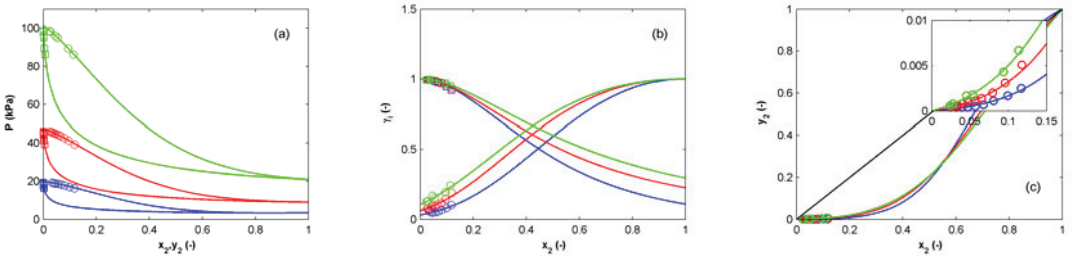


Figure 4. Model prediction for (a) PTxy data [12], (b) Activity coefficients and (c) x/y data of the Pz/$H_2O$ system at 60 C, 80 C and 100 C.

It should be noted that the given parameters (Table 2) do not predict well the binary VLE data [11] at higher concentrations as seen in Fig. 5a as well as reported vapor pressure data in Fig. 5b. However, the model predicts well the freezing point depressions [18] in Fig 5c. The main reason for this is that the parameters were only regressed with low concentration data and for a limited temperature range. This suggests that the parameters could be improved by using more data points into the parameter regression.

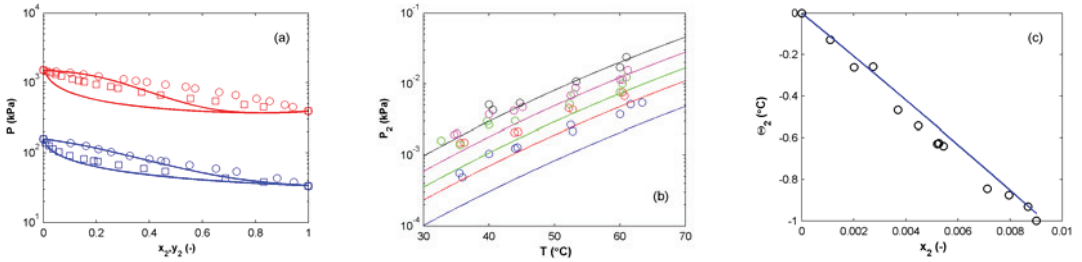


Figure 5. Model prediction for (a) PTxy data at Isothermal measurements at 112.9 C and 198.8 C [11], (b) Vapor pressure of Pz at different concentrations [10] and (c) Freezing point depression [18].

### *3.3. Ternary VLE of AMP(1)/Pz(2)/$H_2O$(3) model*

Fig. 6 shows predictions of activity coefficients for the ternary AMP(1)+Pz(2)+H2O(3) system only using the calculated interaction parameters from the two binary solutions without a new binary interaction between AMP(1) and Pz(2). The model still predicts the ternary VLE system data [12] successfully for AMP. However, the model under-predicts the activity coefficients for Pz. It should be noted that there is much scatter in the data.

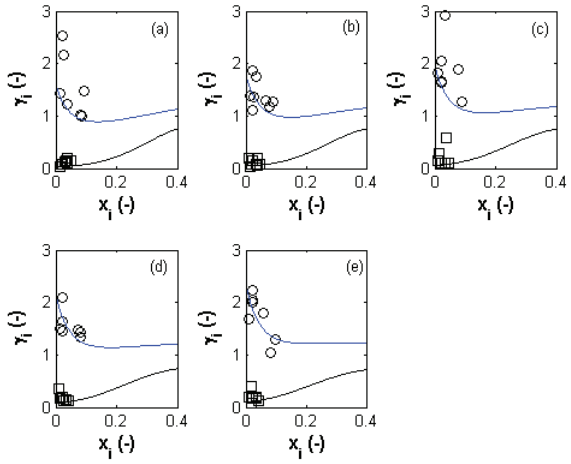


Figure 6. Predictions of activity coefficients for the ternary AMP/Pz/H2O system [12] (a) 60 C, (b) 70 C, (c) 80 C (d) 90 C, and (e) 100 C.

The available freezing point depression data [18] for the ternary system are plotted together with the model in Fig. 7 and it seen that the model gives a reasonable representation of the data apart from at the highest concentrations.

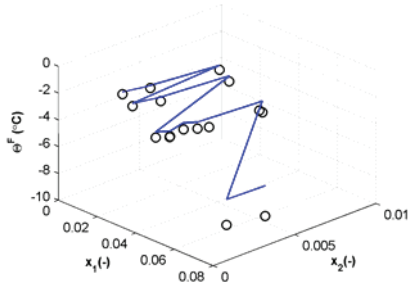


Figure 7. The freezing point depression data [18] and the prediction model (Point, data and solid lines, the NRTL model)

### *3.4. Thermodynamic consistency*

Thermodynamic consistency tests were performed by plotting experimental and model data in parity plots. As seen in Fig. 8a, b, c and d the binary data are consistent, but the ternary data depart significantly from the model and therefore the calculated activity coefficients show larger uncertainties, especially for Piperazine (Pz). It should be noted that the experimental uncertainty in PTxy data is normally large, in particular regarding the y-values.

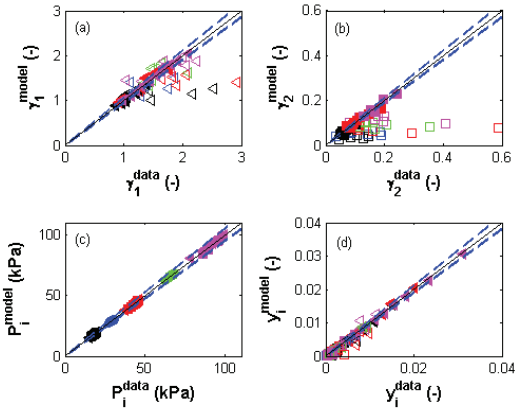


Figure 8. Parity plots for (a) Activity coefficients of AMP, (b) Activity coefficients of Pz, (c) Total pressure ($P_i$), and (d) Vapor phase ($y_i$) for binary and ternary data ( , AMP; h , Pz; Filled Point, Binary data of AMP and Pz; Unfilled Point, Ternary data; black, 60 C; blue, 70 C; red, 80 C; green, 90 C; Magenta, 100 C; and solid lines, diagonal; Dashed line, +/-5% uncertainty).

## 4. Conclusion

An NRTL model was developed to represent binary VLE data of aqueous AMP and Pz solutions and ternary VLE for aqueous AMP/Pz solutions at different temperatures and concentrations. The model represents well the experimental results used for regression and for AMP, also most data available and not used in the regression. From the standard deviations of the parameters it is clear that the model can be significantly improved by fitting to more data. The model shows that the activity coefficients of AMP are much higher than those of Pz. The suggested binary interaction parameters were found to reasonably well predict the ternary AMP/Pz/Water system.

## Acknowledgements

Direct financial support from DNV (Det Norske Veritas AS) and the CCERT project is greatly appreciated. The CCERT project is supported by the Research Council of Norway (NFR 182607), Shell Technology Norway AS, Metso Automation, Det Norske Veritas AS, and Statoil AS.

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